Small angle scattering studies of ordered organosilicate composites

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Introduction

Nanostructured organosilicates with controlled morphologies have been the subject recent interest for many potential applications, including nanopatterning [1], resulting in materials with applications in microelectronics and photonics. One approach to creating ordered nanostructures is to use block copolymers as templates by taking advantage of microphase separation. The structures formed by this process have been studied in a range of systems in which the chemical composition and resulting structure can be related through a phase diagram including ordered cylindrical and lamellar structures and disordered aggregations of spheres. Robust silicate nanostructures can be formed by swelling these highly reproducible phases with silicate precursors that can be cured at temperatures below the melting points of the ordered phases. Small angle X-ray scattering (SAXS) is an important tool for investigating these materials at each stage of their formation.

Methods and Materials

A series of samples was formed by casting and curing mixtures of silicate precursors with solutions polybutadiene and poly(ethylene oxide) into films 100 to 200 μm thick. The structure of samples produced with a variety of compositions and preparations [2] were studied by SAXS. The samples were examined under ambient conditions at the end of the chemical process and showed no signs of degradation following moderate x-ray exposure. Small angle scattering diffraction patterns were obtained by illuminating the sample with a 0.15 to 0.5 mm-diameter incident beam of 10 keV x-rays. The scattered photons were imaged by a liquid nitrogen-cooled charge coupled device camera at a distance of 75 cm from the sample.

Results

The small angle scattering experiments show that the microstructure and phase behavior of these nanocomposites are very sensitive to the polymer-matrix interface and their compositions. These observations are consistent with results obtained from transmission electron microscopy and nuclear magnetic resonance measurements [2]. However, for a range of compositions the diffraction pattern consisted of sharp crystalline reflections that are consistent with the formation of a well-ordered structure with lattice constants of 10 to 20 nm. One such pattern from a phase that can be described with a 2D distorted hexagonal lattice of cylindrical structures is shown in Fig. 2. In this case, the casting and curing process resulted in the long axes of the cylinders lying in the plane of the sample.

No crystalline reflections were observed with the incident beam along the surface normal of the cast film.

Discussion

The sharp reflections seen in Figure 2 are a clear sign of long range order in the organosilicate composites made by swelling block copolymers. Among the challenges for further experiments is to elucidate the origin of the anisotropic structure evident in the distortion of the hexagonal diffraction pattern.

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References

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FIG. 1. Ordered organosilicate structures can be formed by adding silicate precursors to structures formed by a block copolymer process.

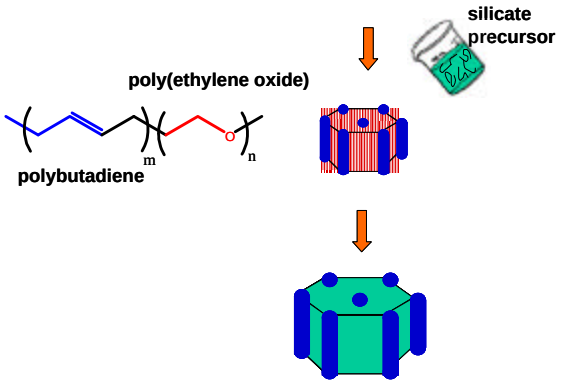

FIG. 2. Small angle x-ray scattering diffraction pattern obtained from an ordered organosilicate composite material. The bright spots are crystalline reflections from the ordered structure. The white vertical streak and dark horizontal band are the an image artifact and the Pb-wire beamstop respectively.